Photocatalytic decomposition of a perfluoroether carboxylic acid by tungstic heteropolyacids in water

Hisao Hori [a],*, Ari Yamamoto [a], Kazuhide Koike [a], Shuzo Kutsuna [a], Misako Murayama [a], Arifumi Yoshimoto [b], Ryuichi Arakawa [b]

[a] *National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba West, 16-1 Onogawa, Tsukuba 305-8569, Japan*
[b] *Department of Applied Chemistry, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan*

Abstract

The photochemical decomposition of perfluoroether carboxylic acid $C_2F_5OC_2F_4OCF_2COOH$ (EEA), which is being introduced in industry as a surfactant alternative to environmentally persistent and bioaccumulative perfluorocarboxylic acids, was investigated by use of water-soluble tungstic heteropolyacids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, and the results were compared with those of conventional techniques, UV–visible light irradiation in the presence of H_2O_2, treatment with Fenton's reagent, and heterogeneous TiO_2 photocatalyst. $H_4SiW_{12}O_{40}$ induced little photochemical decomposition of EEA. Irradiation with UV–visible light in the presence of H_2O_2 and treatment with Fenton's reagent also led to little decomposition of EEA. Alternatively, irradiation of EEA at wavelengths of >290 nm in the presence of $H_3PW_{12}O_{40}$ under an oxygen atmosphere efficiently decomposed EEA to F^- and CO_2. The reaction followed pseudo-first-order kinetics, and the decomposition rate was almost identical with that of the corresponding perfluorocarboxylic acid, that is, $C_5F_{11}COOH$. The proposed reaction mechanism involves redox reactions between EEA, the heteropolyacid catalyst, and oxygen, followed by C–C bond cleavage between $C_2F_5OC_2F_4OCF_2$ and COOH (induced by the photo-Kolbe mechanism), and subsequent formation of $C_2F_5OCF_2COOH$ and trifluoroacetic acid. EEA was also photocatalytically decomposed by TiO_2 with a rate constant comparable with that by $H_3PW_{12}O_{40}$. Although the reactivity of TiO_2 toward perfluorocarboxylic acids was reported to be very low, EEA, which has ether linkages in the perfluoroalkyl chain, was clearly decomposed to F^- and CO_2. This fact suggests that oxidative active species other than OH radicals significantly participate in the reaction.

1. Introduction

Perfluorocarboxylic acids (PFCAs) such as perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) have recently received much attention because they are ubiquitous environmental contaminants [1–3]. These compounds have been widely used as products or as raw materials for surfactants: for example, they are used as emulsifying agents in fluoropolymer manufacture, surface treatment agents for electronic materials, and additives for paintings and waxes, owing to their high surface active effect, high thermal and chemical stability, and high light transparency [2]. After it became clear that PFOA and related chemicals persist and bioaccumulate in the environment, efforts to eliminate these chemicals from products and facility emissions were begun [4]. In addition, alternatives to PFCAs have been being developed. The main strategy for the design of alternatives is to shorten the perfluoroalkyl moiety in the molecules [5], because the length of perfluoroalkyl chain has a large impact on bioaccumulation; compounds with shorter chains are less bioaccumulative [6–8].
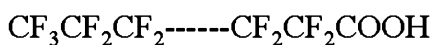
Perfluoroether carboxylic acids are representative alternatives to PFCA-based surfactants [9,10]. In these molecules, ether linkages are inserted in the perfluoroalkyl chain of PFCAs so that the molecules contain only short perfluoroalkyl ($\leq C_4$) groups (Scheme 1).

These chemicals are likely to decompose more easily than PFCAs, owing to the presence of ether linkages. However, the decomposition of perfluoroether carboxylic acids has not been reported; that is, no one has confirmed that these chemicals decompose more easily than conventional PFCAs.

* Corresponding author. Tel.: +81 29 861 8161; fax: +81 29 861 8866.
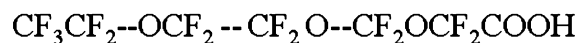*E-mail address:* h-hori@aist.go.jp (H. Hori).

Conventional PFCAs

$$CF_3CF_2CF_2\text{------}CF_2CF_2COOH$$

Perfluoroalkyl chain

Ether linkages are inserted in the perfluoroalkyl chain

Perfluoroether carboxylic acids

$$CF_3CF_2\text{--}OCF_2\text{--}CF_2O\text{--}CF_2OCF_2COOH$$

Short perfluoroalkyl ($\leq C_4$) groups

Scheme 1. PFCAs and perfluoroether carboxylic acids.

PFCAs are only slightly decomposed by conventional techniques for organic pollutants in water such as treatment with Fenton's reagent ($Fe^{2+} + H_2O_2$) [11] and irradiation with UV–visible light in the presence of H_2O_2 [12], because the reactivity of OH radicals with PFCAs in water is low [13,14]. In accordance with the low reactivity of OH radicals toward PFCAs, Mas et al. showed that the most simple PFCA, i.e., trifluoroacetic acid (CF_3COOH, TFA) was not decomposed by TiO_2 photocatalysis [15], and Dillert et al. observed that heptafluorobutyric acid (C_3F_7COOH) was gradually degraded upon UV irradiation in the presence of TiO_2, but the photonic efficiency was very low ($<1 \times 10^{-5}$) [16]. Alternatively, PFCAs are efficiently decomposed to F^- ions and CO_2 by the water-soluble heteropolyacid photocatalyst $H_3PW_{12}O_{40}\cdot6H_2O$ (**1**) [12,17–19], by the persulfate ($S_2O_8^{2-}$) photochemical oxidant [20–22], and by the Fe^{3+} photocatalyst [23]. Water-soluble heteropolyacids are attractive for photocatalysts for the decomposition of PFCAs and related chemicals because of their multielectron capabilities and high stability under highly acidic conditions [24,25], and the oxidation potential of $[PW_{12}O_{40}]^{3-}$ (**1** dissociates into $[PW_{12}O_{40}]^{3-}$ and H^+ in an aqueous solution), is estimated to be more positive than that of TiO_2 [26]. The F^- ions have well-established treatment processes: addition of a calcium salt results in the formation of environmentally harmless CaF_2, a raw material for hydrofluoric acid, the global demand for which is increasing. Development of a system for the decomposition of fluorochemicals is important because such a system would not only reduce the environmental impact of these chemicals but also provide a method for the recycling of a fluorine resource.

We report herein the photochemical decomposition of a perfluoroether carboxylic acid $C_2F_5OC_2F_4OCF_2COOH$ (EEA), a typical PFCA alternative, catalyzed by tungstic hetero-polyacid **1**. For comparison, another water-soluble hetero-polyacid, i.e., $H_4SiW_{12}O_{40}\cdot24H_2O$ (**2**), treatment with Fenton's reagent, UV–visible irradiation in the presence of H_2O_2, and UV–visible irradiation in the presence of TiO_2, were also

examined. The decomposition behavior of EEA by use of **1** was compared with that of the corresponding PFCA having no ether linkages, undecafluorohexanoic acid ($C_5F_{11}COOH$, UFHA). This is the first report of the photochemical decomposition of a perfluoroether carboxylic acid.

2. Experimental

2.1. Materials

Heteropolyacid **1** was obtained from Nippon Inorganic Chemical Co. (Tokyo, Japan). It was purified by ether extraction and recrystallized from water, because a trace amount of impurity affects the reaction rates [27]. The ^{31}P NMR and UV–visible spectral parameters of the purified species (-14.8 ppm in D_2O, relative to 85% H_3PO_4; $\varepsilon = 4.80 \times 10^4 M^{-1} cm^{-1}$ at $\lambda_{max} = 265$ nm in 0.03 M $HClO_4$) were in good agreement with literature values [24,25]. Heteropolyacid **2** ($>99\%$) was obtained from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Powdered TiO_2 (Degussa P25; anatase/rutile ratio, 80:20; BET surface area, 50 $m^2 g^{-1}$) was obtained from Nippon Aerosil Co. (Tokyo, Japan) and used as received. Difluoro[1,1,2,2-tetrafluoro-2-(pentafluoroethoxy)ethoxy] acetic acid (undecafluoro-3,6-dioxaoctanoic acid, $C_2F_5OC_2F_4OCF_2COOH$, EEA, 99%) was obtained from Asahi Glass Company (Tokyo, Japan). TFA ($>99.0\%$), pentafluoropropionic acid (C_2F_5COOH, $>98\%$), heptafluorobutyric acid (C_3F_7COOH, $>99\%$), nona-fluoropentanoic acid (C_4F_9COOH, $>98\%$), and UFHA ($>98\%$) were purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan). Oxygen (99.9%) and Ar (99.99%) gases were purchased from Tomoe Shokai Co. (Tokyo, Japan). Standard gas mixtures, CO_2 (1.010%)/N_2, CF_3H (512 ppmv)/N_2, and CF_4 (500 ppmv)/N_2, were obtained from Takachiho Trading Co. (Tokyo, Japan).

2.2. Photochemical procedures

A cylindrical pressure-resistant Inconel reactor (176-ml volume, 5.9-cm i.d.) equipped with a sapphire window (4.0-cm i.d.) was used. A gold vessel (105 ml, 5.5-cm i.d.), which is stable to highly acidic solutions, was inserted into the reactor. In a typical photocatalytic run, a 0.03 M $HClO_4$ solution (22 ml) containing **1** (11.0 μmol; 0.50 mM) and EEA (111 μmol; 5.05 mM) was poured into the gold vessel. The 0.03 M $HClO_4$ solution was used to keep the reaction solution at pH 1.7, because the anion part of **1**, $[PW_{12}O_{40}]^{3-}$, is unstable above pH 2 [27]. After the reactor was pressurized to 0.49 MPa with oxygen gas, the solution, with stirring, was irradiated with UV–visible light (wavelengths >290 nm) from a xenon–mercury lamp (200 W, L2001-01L, San-Ei Electric Co., Osaka, Japan) through a cutoff filter (UV-30, Kenko Co., Tokyo, Japan). The reactions were also carried out with 313-nm monochromatic light, by means of a band-pass filter (MC313, Asahi Spectra, Tokyo, Japan) combined with the irradiation system. The incident light intensity was determined with a $K_3[Fe(C_2O_4)_3]$ actinometer. The apparent quantum yield for the decomposition of EEA was determined from the following equation:

[(decomposition rate of EEA)/(light intensity)], where the decomposition rate of EEA was determined from data obtained during the short period of irradiation when the amount of EEA decreased linearly with irradiation time.

In all runs, the reaction temperature was held constant at 25 °C. After irradiation, the pressure was released and the gas in the reactor was collected in a sampling bag (CEK-3, GL Sciences, Tokyo, Japan) and subjected to GC–MS and GC measurements. The reaction solution was analyzed by HPLC, ion chromatography, ion-exclusion chromatography, and electrospray ionization (ESI) mass spectrometry. Control reactions without **1** and without oxygen gas (i.e., argon gas was used) were also carried out. Reactions using **1** and UFHA were also performed under the same conditions as the reactions of EEA, except that UFHA was used. Reactions using **2** and EEA were also performed under the same conditions as the reaction using **1**, except that **2** was used.

Photochemical decomposition of EEA by UV–visible irradiation in the presence of H_2O_2 was also investigated: the reaction procedure was almost identical with that used for **1**, except that H_2O_2 (1.00 M) was used. Fenton's reagent was also employed to attempt to decompose EEA, referring to a reported method for PFOA [11]. A 0.03 M $HClO_4$ solution (22 ml) containing EEA (5.27 mM), H_2O_2 (1.00 M), and $FeSO_4 \cdot 7H_2O$ (5.01 mM) was mixed in an oxygen atmosphere (initial pressure, 0.49 MPa) for 12 h in the dark. Photochemical decomposition of EEA induced by TiO_2 was also examined. The procedure was almost identical with that used for **1**, except that TiO_2 powder (3.0 mg; 137 mg l^{-1}) was used. A mixture of 0.03 M $HClO_4$ solution of EEA and TiO_2 was stirred for 1 h, and then irradiated with stirring. After the reaction, the gas in the reactor was collected and subjected to measurement. The resulting liquid–solid mixture was centrifuged, and the solution phase was subjected to measurement.

To measure the changes in the UV–visible spectrum of the reaction solution containing **1** and EEA during irradiation, a photochemical quartz cell (9.6 ml) with an aqueous solution (4.0 ml) containing **1** (5.0 mM) and EEA (15 mM) was irradiated (>290 nm light) under an oxygen or argon atmosphere at normal pressure; the high concentrations of **1** and EEA allowed us to clearly observe the formation of the reduced complex of **1**, $[PW_{12}O_{40}]^{4-}$, in the reaction solution during irradiation under an argon atmosphere.

2.3. Analysis

EEA and UFHA in the reaction solutions were quantified with an HPLC system consisting of an automatic sample injector (injection volume, 30 μl), a degasser, a pump, a guard column, a separation column (Tosoh TSKgel Super ODS, 4.6 mm i.d., 10-cm length ×2, Tosoh, Tokyo, Japan), a column oven, and a conductivity detector. The mobile phase was a mixture of 65:35 (v/v) methanol and aqueous NaH_2PO_4 (20 mM, adjusted to pH 3.0 with H_3PO_4). C_4F_9COOH formed during the decomposition of UFHA was also quantified in the same manner. The F^- concentrations were measured with an ion chromatograph system (Tosoh IC-2001) consisting of an

automatic sample injector (injection volume, 30 μl), a degasser, a pump, a guard column, a separation column (Tosoh TSKgel Super IC-Anion, 4.6-mm i.d., 1.0-cm length), a column oven, and a conductivity detector with a suppressor device. The mobile phase was an aqueous solution containing $Na_2B_4O_7$ (6 mM), H_3BO_3 (15 mM), and $NaHCO_3$ (0.2 mM). Short-chain PFCAs (TFA, C_2F_5COOH, and C_3F_7COOH) were quantified with an ion-exclusion chromatograph system consisting of a guard column, a separation column (Tosoh TSKgel OApak-P, 7.8-mm i.d., 30-cm length), a pump, a column oven, and a conductivity detector. The mobile phase was aqueous phthalic acid (10 mM).

Negative-ion ESI mass spectrometry was used to identify the products in the reaction solution. The system was a TSQ 7000 triple-stage quadrupole mass spectrometer (Thermo Electron Corp., San Jose, CA, USA). The electrospray potential was −4.5 kV against the counter electrode of a heated (200 °C) capillary. Reaction solutions were diluted with water (20-fold by volume) and then with methanol (25-fold by volume), and the diluted solutions were electrosprayed at a flow rate of 10 μl min^{-1}.

Attenuated total reflectance (ATR)-IR spectra were measured for the reaction solutions to observe whether degradation of catalyst **1** occurred during reactions. The measurement was carried out with a FTIR spectrometer (MB106, Bomen, Québec, Canada) with a HgCdTe detector and a diamond ATR cell (DuraSamplIR II, S.T. Japan, Tokyo, Japan). The reaction solutions were subjected to measurement without dilution.

The gas-phase products were identified with a GC–MS system consisting of a gas chromatograph (HP5890, Hewlett-Packard, Wilmington, DE, USA) with a column (Poraplot Q, 0.32-mm i.d., 25-m length, Chrompack, Bergen op Zoom, The Netherlands), a mass spectrometer (HP 5972A), and a workstation (HP G1034CJ). The carrier gas was He, and the sample gas volume was 30 μl. The electron impact source was operated at 70 eV. The analyses were conducted in full scan mode (m/z 1.2–200), and the detection limit for CHF_3 calculated from a signal-to-noise ratio of 3, was 0.56 ppmv based on the intensity at m/z 51, and that for CF_4 was 0.25 ppmv based on the intensity at m/z 69.

CO_2 was quantified on a GC (GC 323, GL Sciences) with an active carbon column. Changes in the UV–visible spectra during irradiation were measured with a multichannel spectrophotometer (MCPD-1000, Otsuka Electronics Co., Osaka, Japan), connected to the photochemical cell by optical fibers.

3. Results and discussion

3.1. Photocatalytic decomposition of EEA by **1**

Under our reaction conditions, an acidic aqueous solution containing catalyst **1** and EEA was irradiated with UV–visible light from a xenon–mercury lamp through a UV-30 cutoff filter. With this filter in place, the lamp emits light at wavelengths above 290 nm (Fig. 1). EEA has no absorption above 230 nm, whereas **1** has strong absorption in the deep UV region to
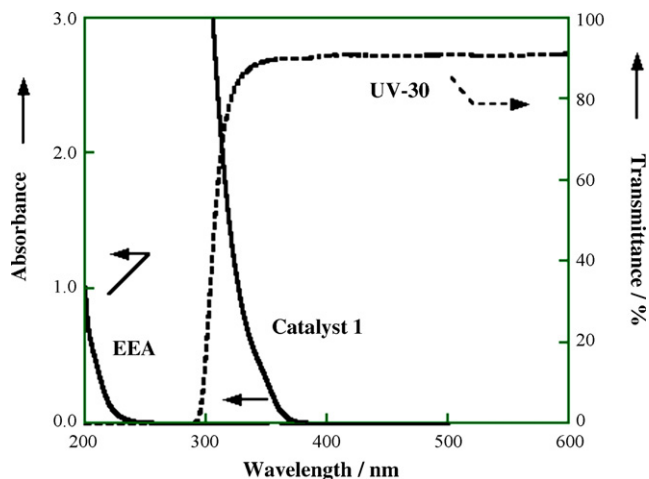
Fig. 1. UV–visible absorption spectra of EEA (5.05 mM) and catalyst **1** (0.50 mM) in 0.03 M HClO$_4$ and the transmittance of the UV-30 cutoff filter. Concentrations of EEA and **1** are the same as those used in the catalysis experiment (see Fig. 2). The path length for the absorption spectrum measurements was 1.0 cm.

approximately 390 nm. Hence, **1** is the only species that can absorb the light from the lamp during the photochemical reactions.

The irradiation-time dependence of the photoreaction in which we used a 10-fold molar excess of EEA relative to **1** is shown in Fig. 2. As expected, the amount of EEA decreased with irradiation time, and F$^-$ and CO$_2$ were the major products in the aqueous and gas phases, respectively. The decomposition of EEA followed pseudo-first-order kinetics with a rate constant of 1.15×10^{-1} h^{-1}. After 12 h of irradiation, 69.1% of the initial EEA was decomposed, corresponding to a turnover number [(moles of decomposed EEA)/(moles of initial **1**] of 6.97. The yields of F$^-$ [(moles of formed F$^-$)/(moles of fluorine
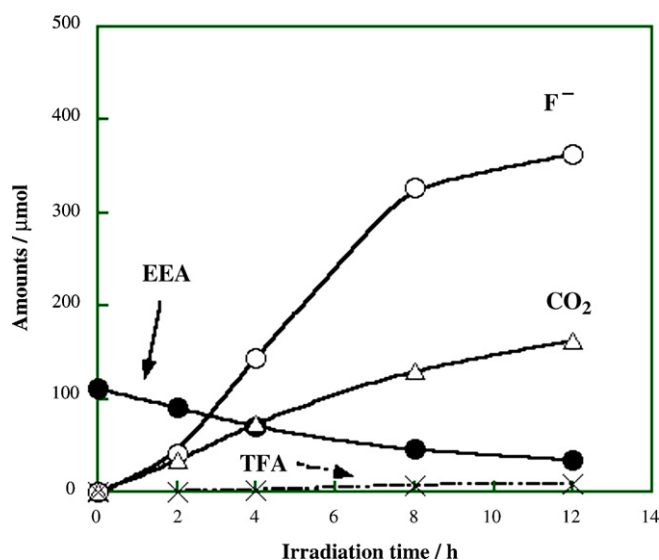

Fig. 2. Irradiation-time dependence of EEA decomposition catalyzed by **1**. A 0.03 M HClO$_4$ solution (22 ml) containing **1** (11.0 µmol; 0.50 mM) and EEA (111 µmol; 5.05 mM) was irradiated (>290 nm light) under an oxygen atmosphere (0.49 MPa).

content in initial EEA, i.e., moles of initial EEA $\times$ 11)] and CO$_2$ [(moles of formed CO$_2$)/(moles of carbon content in initial EEA, i.e., moles of initial EEA $\times$ 6)] were 29.7% and 24.3%, respectively. Ion-exclusion chromatography revealed the formation of a small amount of TFA, and the amount slightly increased with irradiation time (Fig. 2). Other PFCAs, i.e., C$_2$F$_5$COOH, and C$_3$F$_7$COOH, were not detected. GC–MS analysis of the gas phase revealed that the reaction system produced no environmentally undesirable greenhouse gases such as CF$_4$ and CF$_3$H. The ATR-IR spectrum of the reaction solution after 12 h of irradiation showed absorption maxima at 1080 and 982 cm^{-1}, corresponding to the P–O and W=O stretching modes, respectively [25], and the spectral feature was the same as that before irradiation: there was no sign of the degradation of **1**, such as degradation to lacunary polyanion PW$_{11}$O$_{39}$$^{7-}$, which has the absorption maxima at 1085 and 1040 cm^{-1} for P–O and 950 cm^{-1} for W–O stretching modes [25].

The product distributions obtained under various reaction conditions are listed in Table 1. In the absence of light irradiation, no reaction occurred (Table 1, entry 2): the concentration of EEA in the reaction solution was the same as that in the absence of **1** under dark, indicating that the decrease of EEA concentration owing to the interaction between EEA and **1** is negligible for the quantification of EEA. When the reaction was carried out in the absence of either catalyst **1** or oxygen gas, little reaction was observed (entries 3 and 4). The combination of **1**, oxygen, and light irradiation was required for effective EEA decomposition (entry 1). These results clearly indicate that **1** acted as a photocatalyst. The photocatalytic decomposition of EEA was greatly affected by the initial amount of EEA. For a constant amount of **1** and a reaction time of 4 h, the amount of EEA decomposed and the amounts of F$^-$, CO$_2$ and TFA formed all increased as the initial amount of EEA was increased (Table 2). When the initial amount of EEA was increased to 222 µmol [(initial EEA)/(initial **1**) molar ratio = 20/1], the turnover number reached 7.64 after 4 h of irradiation. Consistent with the pseudo-first-order decomposition kinetics for EEA, the ratio of EEA decomposed remained nearly constant (36.6–38.0%) as the initial amount of EEA was varied.

Decomposition of EEA using **1** and oxygen was also observed when the sample solution was irradiated with 313-nm monochromatic light. When the light intensity was 7.77×10^{-4} einstein h^{-1} (1 einstein = 6.022×10^{23} photons) and the initial amount of EEA was a 10-fold excess relative to **1**, the apparent quantum yield for EEA decomposition was measured to be 5.48×10^{-3}.

Although EEA was efficiently decomposed in the presence of **1**, the fluorine recovery after 12 h of irradiation (>290 nm light) [i.e., the molar ratio of total fluorine content after irradiation (=F$^-$ + fluorine in TFA + fluorine in unchanged EEA) to that in EEA before irradiation] was 62.9%. On the other hand, the carbon recovery after 12 h of irradiation (>290 nm light) [i.e., the molar ratio of total carbon content after irradiation (=CO$_2$ + carbon in TFA + carbon in unchanged EEA) to that in EEA before irradiation] was

Table 1
Dependence of the distribution of products from decomposition of EEA on reaction conditions[a]

Entry	Catalyst 1	Light	Atmosphere[b]	EEA decomposed (μmol) [ratio (%)]	F^- (μmol) [yield (%)]	CO_2 (μmol) [yield (%)]	TFA (μmol)
1	Present[c]	Present	O_2	76.7 [69.1]	363 [29.7]	162 [24.3]	9.09
2	Present[c]	None	O_2	ND[d] [0]	ND[d] [0]	ND[d] [0]	ND[d]
3	None	Present	O_2	5.40 [4.86]	10.7 [0.88]	10.8 [1.62]	ND[d]
4	Present[c]	Present	Ar	8.40 [7.57]	5.84 [0.48]	9.39 [1.41]	ND[d]

[a] Reaction time, 12 h; initial EEA amount, 111 μmol; reaction solution volume, 22 ml.
[b] Pressure, 0.49 MPa.
[c] Intial amount of 1, 11.0 μmol.
[d] Not detected.

58.0%. The fluorine and carbon recoveries lower than 100% suggest that another product was present in the reaction solution. In fact, the HPLC chromatogram for the reaction solution after irradiation showed a peak corresponding to an unknown product. The retention time of the peak indicated that this species was not any of the PFCAs, and we supposed it to be a carboxylic acid with a short ($\sim$four atoms) and partly oxygenated (ether linkage) perfluoroalkyl group.

After 12 h of irradiation, the molar amount of the unknown fluorine component was calculated to be 452 μmol [=fluorine content in initial EEA – (fluorine content in remaining EEA + F^- + fluorine content in TFA)], and the molar amount of the unknown carbon component [=carbon content in initial EEA – (carbon content in remaining EEA + CO_2 + carbon content in TFA)] was 279 μmol. Hence, the F/C atomic ratio was 1.62. Therefore, we proposed that the unknown product was $C_2F_5OCF_2COOH$, which has a similar F/C ratio, 1.75.

To conclusively identify this product, we subjected the reaction solutions to ESI–mass spectrometry. Before irradiation, three peaks due to EEA were observed (Fig. 3A): m/z 691, 345, and 251. The peak at m/z 345 corresponds to the EEA anion, $[EEA-H]^-$; and the peaks at m/z 691 and 251 correspond to a dimer $[2 \times EEA-H]^-$ and a fragment species $[C_2F_5OC_2F_4O]^-$, respectively, generated from $[EEA-H]^-$ during the measurements. After 12 h of irradiation, the intensity of $[EEA-H]^-$ was markedly decreased, and the decrease corresponded to the decrease in the EEA concentration in the reaction solution; at the same time, a new peak appeared at m/z 229 (Fig. 3B), which corresponds to

$[C_2F_5OCF_2COO]^-$. Therefore, we identified the unknown product as $C_2F_5OCF_2COOH$.

3.2. Heteropolyacid 2, UV–visible irradiation in the presence of H_2O_2, and treatment with Fenton's reagent

Heteropolyacid 2 has very similar UV–visible spectroscopic feature to that of 1 [28] and was known to work as a photocatalyst to decompose chlorophenols, although the catalytic ability is lower than 1 [29]. We observed that 2 induced very little EEA decomposition: after 12 h of irradiation, only 2.34% of the initial EEA was consumed, accompanying with formation of small amounts of F^- and CO_2 (Table 3, entry 1). This result is contrastive to that for 1 (decomposition ratio: 69.1%, Table 1, entry 1). The lower reactivity of 2 may originate from slower electron transfer

Table 2
Effect of initial amount of EEA on the photocatalytic EEA decomposition by 1[a]

Entry	Initial amount of EEA (μmol)	EEA decomposed (μmol) [ratio (%)]	F^- (μmol)	CO_2 (μmol)	TFA (μmol)
1	57.0	21.7 [38.0]	101	50.3	1.97
2	111	40.6 [36.6]	144	73.7	2.61
3	222	84.0 [37.8]	334	130	4.70

[a] Reaction time, 4 h; reaction solution volume, 22 ml; initial amount of 1, 11.0 μmol; oxygen pressure, 0.49 MPa.
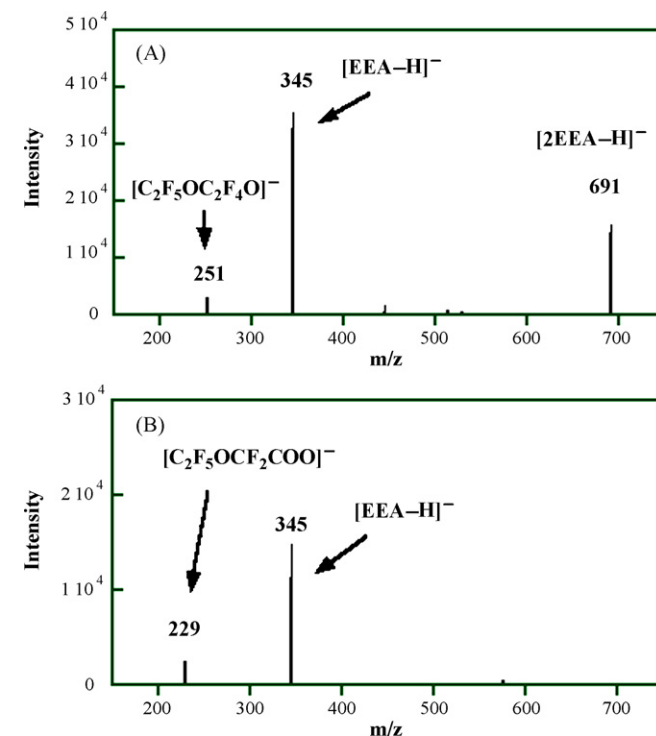

Fig. 3. ESI-mass spectra of the reaction solutions: (A) before irradiation and (B) after 12 h of irradiation. The reaction conditions were the same as those described in Fig. 2.

Table 3
EEA decomposition by **2**, by UV–visible irradiation in the presence of H_2O_2, and by treatment with Fenton's reagent[a]

Entry	Conditions	Initial amount of EEA (μmol)	EEA decomposed (μmol) [ratio (%)]	F^- (μmol) [yield (%)]	CO_2 (μmol) [yield (%)]
1	**2** + >290 nm light[b]	111	2.60 [2.34]	14.9 [1.22]	12.7 [1.91]
2	H_2O_2 (1.00 M) + >290 nm light[c]	115	4.91 [4.27]	6.26 [0.49]	15.8 [2.29]
3	H_2O_2 (1.00 M) + Fe^{2+} (5.01 mM)[d]	116	2.20 [1.90]	1.62 [0.13]	7.57 [1.09]

[a] Reaction time, 12 h; reaction solution volume, 22 ml; initial oxygen pressure, 0.49 MPa.
[b] Initial amount of **2** was 12.6 μmol, and the irradiation light intensity was the same as that for the reaction with **1** (Tables 1 and 2 and Fig. 2).
[c] The initial pH value of the solution was 1.5, and the irradiation light intensity was the same as that used for the reaction with **1** (Tables 1 and 2 and Fig. 2). The pressure was increased from 0.49 to 0.67 MPa by the reaction.
[d] The initial pH value of the solution was 1.8. The pressure after the reaction was 0.61 MPa.

process from EEA to the excited anion complex of **2**, because the estimated oxidation potential of $[SiW_{12}O_{40}]^{4-}$ is more negative than that of $[PW_{12}O_{40}]^{3-}$ [26].

UV–visible irradiation in the presence of H_2O_2 has been used to decompose many organic pollutants in water [30]; under these conditions, the photolysis of H_2O_2 causes OH radicals. Fenton's reagent (Fe^{2+} + H_2O_2) is also frequently used as a source of OH radicals. We attempted to decompose EEA by these techniques. However, UV–visible irradiation in the presence of H_2O_2 resulted in little EEA decomposition: after 12 h of irradiation, only 4.27% of the initial EEA was consumed, and only small amounts of F^- and CO_2 were formed (Table 3, entry 2). Fenton's reagent also resulted in little EEA decomposition: 1.90% of the initial amount of EEA was consumed after 12 h (Table 3, entry 3). These results contrast with the results for decomposition induced by **1**: the decomposition ratio of EEA reached 69.1% after 12 h of irradiation (Table 1, entry 1). The results for UV–visible irradiation in the presence of H_2O_2 and for treatment with Fenton's reagent indicate that EEA is not very reactive with respect to OH radicals; these results agree with results showing that PFOA undergoes little decomposition upon UV–visible irradiation in the presence of H_2O_2 [12] and treatment with Fenton's reagent [11].

3.3. Photocatalytic decomposition of UFHA by 1

The irradiation-time dependence of the decomposition of UFHA catalyzed by **1** under 0.49 MPa of oxygen is shown in Fig. 4. In this experiment, we used a 10-fold molar excess of EEA relative to **1**, that is, the same conditions used for EEA (Fig. 2). As expected, UFHA decomposed to F^- and CO_2 (Fig. 4A) and small amounts of short-chain PFCAs (Fig. 4B), as is the case for other PFCAs we have reported previously [12,18,19]. After 12 h of irradiation, 70.5% of the initial EEA was decomposed, and the turnover number reached 7.11. These values are similar to those for EEA after the same irradiation time (decomposition ratio, 69.1%, turnover number, 6.97). The decomposition of UFHA followed pseudo-first-order kinetics with a rate constant of 1.04×10^{-1} h^{-1}, which is similar to the value of EEA (1.15×10^{-1} h^{-1}). Furthermore, when the light intensity was 7.77×10^{-4} einstein h^{-1} and the initial amount of UFHA was in a 10-fold excess relative to the amount of **1**, the apparent quantum yield for UFHA decomposition induced by

313-nm irradiation was 5.97×10^{-3}, which is similar to the value for EEA (5.48×10^{-3}). These facts suggest that the initial decomposition step is the same for these two compounds, that is, that the position of the first bond cleavage is the same in the two compounds. In agreement with the results for EEA, UFHA decomposition induced by irradiation at >290 nm in the presence of **1** was suppressed when the reaction was carried out under an argon atmosphere (0.49 MPa): the decomposition ratio of UFHA was 7.49% after 12 h of irradiation, which is much lower than the value under an oxygen atmosphere (70.5%).

3.4. Reaction mechanism of EEA decomposition by 1

The anion part of **1**, $[PW_{12}O_{40}]^{3-}$, is stable below pH 2, but at higher pH values, it is partly converted to $[PW_{11}O_{39}]^{7-}$ [27].
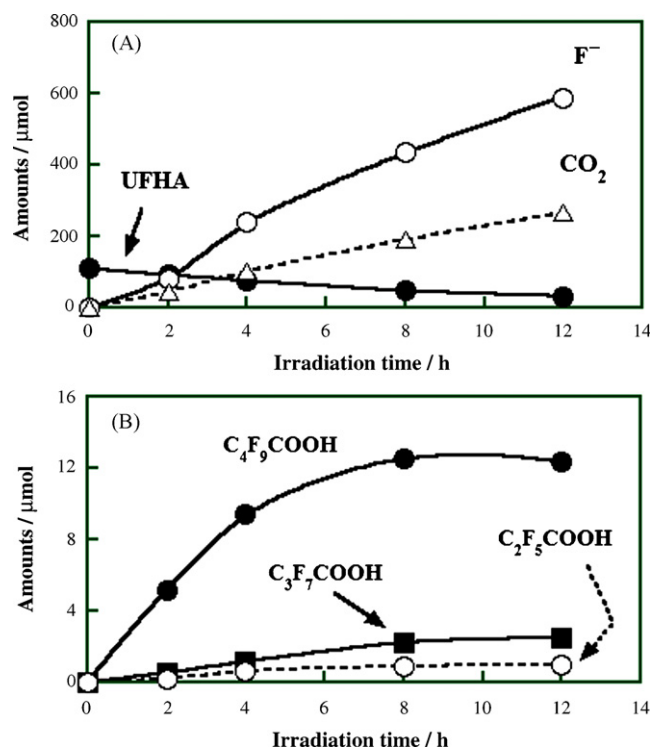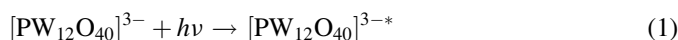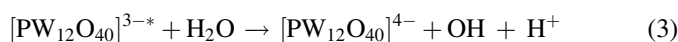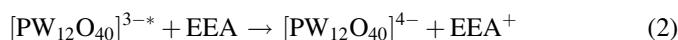

Fig. 4. Irradiation-time dependence of UFHA decomposition catalyzed by **1**: (A) consumption of UFHA and formation of F^- and CO_2 and (B) formation of short-chain PFCAs. The reaction conditions were the same as those described in Fig. 2, except that UFHA was used instead of EEA.

In the present system, the pH of the reaction solutions was kept nearly constant (pH ∼1.7); therefore, $[PW_{12}O_{40}]^{3-}$ was stable during the reactions. The proposed mechanism for the decomposition of EEA is as follows. Photoexcitation of the ground-state species to the ligand-to-metal charge-transfer excited-state complex, $[PW_{12}O_{40}]^{3-*}$, is generally accepted as the initiation process of photocatalysis by **1** [24,25] (Eq. (1)):
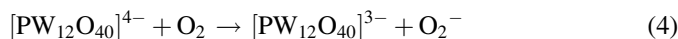
$$[PW_{12}O_{40}]^{3-} + h\nu \rightarrow [PW_{12}O_{40}]^{3-*} \tag{1}$$

There are two plausible processes for the reaction of $[PW_{12}O_{40}]^{3-*}$: electron transfer from EEA to the excited-state complex (Eq. (2)) and electron transfer from water to form OH radicals (Eq. (3)).

$$[PW_{12}O_{40}]^{3-*} + EEA \rightarrow [PW_{12}O_{40}]^{4-} + EEA^+ \tag{2}$$

$$[PW_{12}O_{40}]^{3-*} + H_2O \rightarrow [PW_{12}O_{40}]^{4-} + OH + H^+ \tag{3}$$

Kormali et al. reported that OH radicals generated from Eq. (3) act as major oxidants in the photodegradation of 4-chlorophenol and dichlorophenoxyacetic acid induced by $[PW_{12}O_{40}]^{3-}$, on the basis of the effects of OH radical scavengers on the photoreactions of these substrates [31]. However, in our case, OH radicals seem not have played an important role in the initial decomposition step of EEA, because EEA underwent minimal decomposition when subjected to UV–visible irradiation in the presence of H_2O_2 and to treatment with Fenton's reagent, as described above. Therefore, the electron transfer from EEA to $[PW_{12}O_{40}]^{3-*}$ (Eq. (2)) is likely to have been the major pathway for catalytic EEA decomposition.

$[PW_{12}O_{40}]^{3-*}$ relaxes very rapidly: the emission lifetime of sodium and tetrapropylammonium salts of $[PW_{12}O_{40}]^{3-}$ in water is 1.5 ± 0.5 ns [32]. Nevertheless, the excited state is quenched by small quantifies (10^{-3} M) of alcohol, because of a static mechanism based on the precomplexation of $[PW_{12}O_{40}]^{3-}$ and alcohol [32]. The enhancement of the decomposition amount of EEA proportional to the increase in the initial amount of EEA (Table 2) in our study supports that the idea that precomplexation of $[PW_{12}O_{40}]^{3-}$ with EEA is necessary for the subsequent reaction of $[PW_{12}O_{40}]^{3-*}$ with EEA. After electron transfer from EEA to $[PW_{12}O_{40}]^{3-*}$ (Eq. (2)), the resulting reduced complex, $[PW_{12}O_{40}]^{4-}$, is oxidized to $[PW_{12}O_{40}]^{3-}$ (Eq. (4)):

$$[PW_{12}O_{40}]^{4-} + O_2 \rightarrow [PW_{12}O_{40}]^{3-} + O_2^- \tag{4}$$

In the absence of oxygen, the oxidation process of the reduced complex is very slow. In fact, when the photoreaction was carried out under an argon atmosphere, conditions under which very little EEA decomposition occurred, the UV–visible spectra showed the appearance of a broad absorption in the region from 400 to 800 nm, with absorption maxima at 493 and 752 nm (Fig. 5). The new absorption reflects the appearance of one-electron-reduced complex, $[PW_{12}O_{40}]^{4-}$, which was identified by its reported spectrum [28]. In contrast, when the photoreaction was carried out under oxygen, which allowed efficient EEA decomposition, the spectrum after irradiation
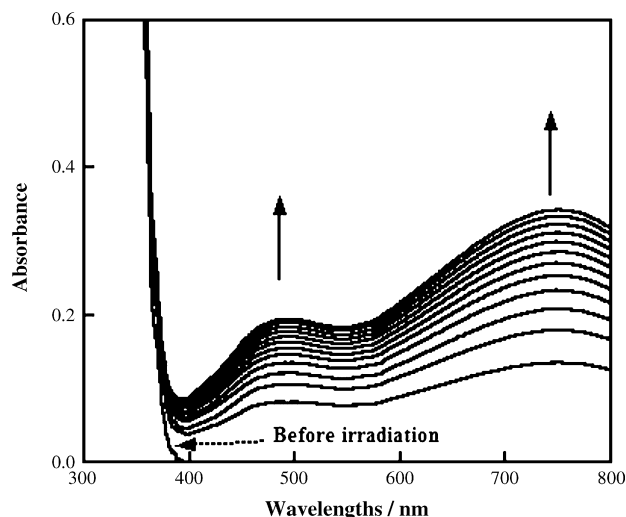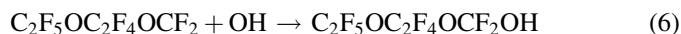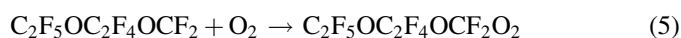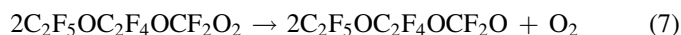

Fig. 5. Changes in the UV–visible absorption spectra of an aqueous solution containing **1** (5.0 mM) and EEA (15 mM) during irradiation (>290 nm light) under an argon atmosphere (recorded at 5-min intervals).

was the same as that before irradiation, and no near-IR absorption was observed. These facts indicate that oxygen was effectively used in the oxidation of $[PW_{12}O_{40}]^{4-}$.

After electron transfer between $[PW_{12}O_{40}]^{3-*}$ and EEA (Eq. (2)), the first bond to be cleaved in the one-electron-oxidized EEA may be the C–C bond between $C_2F_5OC_2F_4OCF_2$ and COOH. This cleavage produces $C_2F_5OC_2F_4OCF_2$ radicals and CO_2, probably by the photo-Kolbe mechanism, which has been proposed as the mechanism for the decomposition of acetic acid by a polyoxomolybdate [33] and the mechanism for the decomposition of PFCAs by **1** [12,17–19]. The $C_2F_5OC_2F_4OCF_2$ radicals in water can undergo reaction with O_2 (Eq. (5)) and reaction with OH (Eq. (6)).

$$C_2F_5OC_2F_4OCF_2 + O_2 \rightarrow C_2F_5OC_2F_4OCF_2O_2 \tag{5}$$

$$C_2F_5OC_2F_4OCF_2 + OH \rightarrow C_2F_5OC_2F_4OCF_2OH \tag{6}$$

Although OH radicals can be produced by the reaction of the excited-state complex with water (Eq. (3)), in the presence of a large amount of O_2, reaction with O_2 (Eq. (5)) should occur more efficiently than reaction with OH (Eq. (6)), because alkyl radicals react with O_2 at diffusion-control rates [34]. In fact, CF_3 radicals are transformed to CF_3O_2 radicals in water [35]. Once formed, the $C_2F_5OC_2F_4OCF_2O_2$ radicals are decomposed to $C_2F_5OC_2F_4OCF_2O$ (Eq. (7)), by means of a reaction similar to the reaction whereby a perfluoroalkyl peroxy radical $C_nF_{2n+1}O_2$ is decomposed to a perfluoroalkoxy radical $C_nF_{2n+1}O$ [36]:

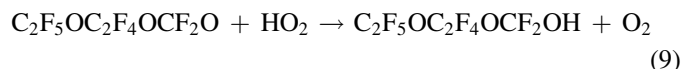$$2C_2F_5OC_2F_4OCF_2O_2 \rightarrow 2C_2F_5OC_2F_4OCF_2O + O_2 \tag{7}$$

On the other hand, HO_2 radicals can be formed from the O_2^- radicals produced in the oxidation process of the reduced complex (Eq. (4)): there is an equilibrium between HO_2 and O_2^- ($pK_a = 4.8$) (Eq. (8)) [37], and because our system is highly

acidic (pH $\sim$1.7), most of the O_2^- should be transformed into HO_2:

$$HO_2 \leftrightarrow O_2^- + H^+ \qquad (8)$$

The $C_2F_5OC_2F_4OCF_2O$ radicals further react with HO_2 to produce $C_2F_5OC_2F_4OCF_2OH$ (Eq. (9)), in a reaction analogous to the reaction of $C_nF_{2n+1}O$ to form perfluoroalkyl alcohol $C_nF_{2n+1}OH$ [38,39]:

$$C_2F_5OC_2F_4OCF_2O + HO_2 \rightarrow C_2F_5OC_2F_4OCF_2OH + O_2 \qquad (9)$$

Conversion of the alkoxy radical to the alcohol (Eq. (9)) might be expected to be induced not only by HO_2 but also by HCO_3^- derived from the CO_2 produced. However, this possibility can be excluded because of the pH ($\sim$1.7) of the reaction solution: because the pK_a for the first dissociation of H_2CO_3 is 3.7 [40], the concentration of HCO_3^- is very low under our conditions.

Similarly to $C_nF_{2n+1}OH$ [39], the thermally unstable alcohol forms acid fluoride $C_2F_5OC_2F_4OCOF$ (Eq. (10)), which is easily hydrolyzed to $C_2F_5OC_2F_4OCOOH$ (Eq. (11)) [41].

$$C_2F_5OC_2F_4OCF_2OH \rightarrow C_2F_5OC_2F_4OCOF + HF \qquad (10)$$

$$C_2F_5OC_2F_4OCOF + H_2O \rightarrow C_2F_5OC_2F_4OCOOH + HF \qquad (11)$$
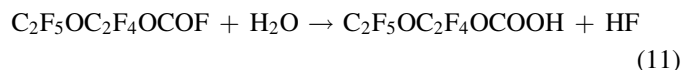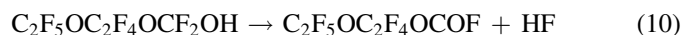
The resulting carboxylic acid $C_2F_5OC_2F_4OCOOH$ is decomposed to $C_2F_5OC_2F_4O$ by **1** via the photo-Kolbe mechanism, and the resulting $C_2F_5OC_2F_4O$ is transformed to $C_2F_5OC_2F_4OH$ by means of reaction with HO_2. $C_2F_5OC_2F_4OCOOH$ may be unstable because it was not observed in the ESI-mass spectra of the reaction solutions. It may easily decompose to $C_2F_5OC_2F_4$ radical, which is transformed to $C_2F_5OC_2F_4OH$ by means of reaction with O_2 and then reaction with HO_2. $C_2F_5OC_2F_4OH$ can be transformed to $C_2F_5OCF_2COF$ in a manner similar to that described above for $C_2F_5OC_2F_4OCF_2OH$. The acid fluoride is hydrolyzed to form $C_2F_5OCF_2COOH$, which was consistently detected in the ESI-mass spectra during the photocatalytic decomposition of EEA by **1** (Fig. 3B).

$C_2F_5OCF_2COOH$ is further decomposed to $C_2F_5OCF_2$ by **1**, and the radical formed may be transformed to C_2F_5OH, via C_2F_5OCOF and C_2F_5OCOOH. The unstable alcohol, C_2F_5OH, is transformed to CF_3COF, which is hydrolyzed to form TFA. We consistently detected TFA in our reaction system, and it can be further decomposed by **1** [17].

3.5. Photocatalytic decomposition of EEA by TiO$_2$

As described in Section 1, the photochemical reactivity of TiO$_2$ toward PFCAs such as TFA [15] and C_3F_7COOH [16] were reported to be very low. The low reactivity is owing to low reactivity of OH radicals toward PFCAs [13–15], and this interpretation is consistent with the facts that PFOA was not decomposed by Fenton's reagent [11] and by UV–visible irradiation in the presence of H_2O_2 [12]. However, EEA has ether linkages in the perfluoroalkyl chain, which has the possibility of different reactivity toward TiO$_2$, from those of
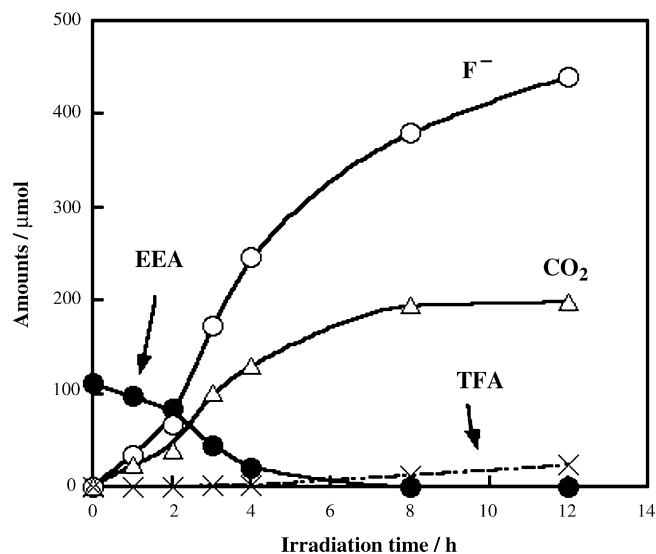

Fig. 6. Irradiation-time dependence of EEA decomposition catalyzed by TiO$_2$. A mixture of 0.03 M HClO$_4$ solution (22 ml) containing EEA (111 μmol; 5.05 mM) and TiO$_2$ (3.0 mg; 137 mg l^{-1}) was irradiated (>290 nm light) under an oxygen atmosphere (0.49 MPa).

PFCAs. Therefore we elucidated the photochemical EEA decomposition induced by TiO$_2$. It should be noted that **1** and **2** in the present work act under homogeneous conditions, whereas TiO$_2$ acts under a heterogeneous condition.

The irradiation-time dependence of the EEA decomposition using TiO$_2$ is shown in Fig. 6, in which we used the same EEA amount as that in the reaction with **1** (Fig. 2). Contrary to expectation from PFCAs, the amount of EEA clearly decreased with irradiation time, and F$^-$ and CO$_2$ were the major products, accompanying with a small amount of TFA. The rate constant for the EEA decomposition in the initial period of irradiation was measured to be 1.38×10^{-1} h^{-1}, which was comparable with that for **1** (1.15×10^{-1} h^{-1}). As described in Section 3.2, EEA showed little decomposition by use of Fenton's reagent and by use of UV–visible irradiation in the presence of H_2O_2 (entries 2 and 3 in Table 3), in which OH radicals play as the active species for the reaction. Therefore, the decomposition of EEA induced by TiO$_2$ observed here suggests that oxidative active species other than OH radicals significantly participate in the reaction.

After 12 h of irradiation, EEA was not detected in the HPLC chromatogram. At this irradiation time, the fluorine recovery was 41.8% and the carbon recovery was 36.8%. These values are lower than those for **1** at 12 h of irradiation (fluorine and carbon recoveries were 62.9% and 58.0%, respectively). The lower fluorine and carbon recoveries by use of TiO$_2$ may indicate that species other than F$^-$, CO$_2$, and TFA largely produce in this system.

4. Conclusion

We investigated the photochemical decomposition of a typical perfluoroether carboxylic acid, $C_2F_5OC_2F_4OCF_2COOH$ (EEA), in water. The hereropolyacid **2**, and conventional techniques, such as UV–visible irradiation in the presence of

H_2O_2 and treatment with Fenton's reagent, led to little decomposition of EEA. In contrast, irradiation with >290 nm light in the presence of heteropolyacid **1** under an oxygen atmosphere efficiently decomposed EEA to produce F^- and CO_2. Although perfluoroether carboxylic acids are believed to decompose more easily than PFCAs, the decomposition rate of EEA induced by **1** was almost identical with that of the corresponding PFCA with no ether linkages, that is, $C_5F_{11}COOH$ (UFHA). This fact supports the idea that these chemicals share the same initial decomposition step. The reaction mechanism involves redox reactions between EEA, **1**, and oxygen, followed by the formation of $C_2F_5OCF_2COOH$ and TFA as intermediates. EEA was also photocatalytically decomposed by TiO_2 with a rate constant comparable with that by **1**. Although the reactivity of TiO_2 toward perfluorocarboxylic acids was reported to be low, EEA was clearly decomposed to F^- and CO_2, suggesting that oxidative active species other than OH radicals significantly participate in the reaction.

Acknowledgements

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